Flexible Minerals

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Bio-Inspired Materials Science at Its Best—Flexible Mesocrystals of Calcite**

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Research into biomineralization[1] serves as an inspiration for scientists by exploring nature's principles and strategies in the design of mineral-based hybrids with outstanding material properties, which have not (yet?) been achieved in man-made counterparts. In biominerals, the inorganic and organic constituents are combined within sophisticated hierarchical structures tailor-made on all levels with respect to strength, flexibility, and biological function.[2] A prominent example is nacre, the inner layer of the shells of different mollusks, which consists of pseudo-hexagonal tablets of aragonite, roughly 10–20 μm wide and 200–500 nm thick, making up approximately 95 % of the biological composite. The platelets are embedded in an organic matrix of mainly chitin and various proteins; as a result the fracture resistance is 3000 times greater than that of the pure mineral. The high toughness essentially relies on the retardation of the propagation of cracks and the dispersion of fracture energy within the organic phase, where biopolymeric adhesives provide sacrificial bonds and hidden lengths.[3] A general observation is that typical length scales of the smallest level of hierarchy in biocomposites lie in the nanometer regime, where imperfections and flaws have been suggested to not affect the material strength.[4] Today, we are still far from utilizing the known design principles of biomaterials in the target-oriented production of synthetic materials. The mechanistic means to control crystallization are not understood, and bottom-up approaches to crystals with complex form, (super-) structure, and tailor-made properties rely on empirical strategies, including the tuning of the underlying organic–inorganic interactions.[5]

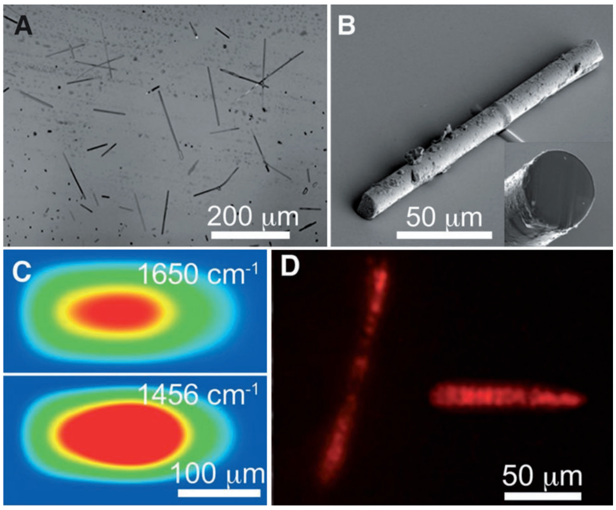

Figure 1. Synthetic calcitic spicules grown in the presence of silicatein-α. A) Overview (light microscopy). B) SEM image of a single spicule and of a cross section (inset) prepared utilizing a focused ion beam. C) Intensities of the amide I band (top, 1650 cm^{-1}) and ν_3 vibrational mode of the carbonate ion (bottom, 1456 cm^{-1}) obtained by FTIR mapping of a single spicule (red indicates highest intensity). D) Immunostained synthetic spicules evidencing the presence of silicatein-α by means of its red fluorescence (confocal microscopy image). From Ref. [6]. Reprinted with permission from AAAS.

Natalio et al.[6] have recently presented a bio-inspired material based on calcium carbonate that encompasses high strength in combination with remarkable flexibility. The self-assembled synthetic spicules of calcite (10–300 μm long and 5–10 μm in diameter, Figure 1) are similar to those seen in the sponge *Sycon* sp., which were utilized as a reference. The synthesis of the artificial spicules relied on the protein silicatein-α, which is important for the formation of siliceous spicules in distinct species of sponges.[7] In this work, silicatein-α formed fibrils that were mineralized with calcium carbonate instead of silica. The initially amorphous calcium carbonate was transformed within five to six months, and the resulting spicules diffracted X-rays like a twinned crystal of calcite. In-depth analyses of the reflections and TEM indicated the presence of crystallographically aligned nano-domains, 5–7 nm in size, rendering the spicules calcite mesocrystals.[8] While the organic content in the biological specimens from *Sycon* sp. was 1.5 %, the synthetic composite fibers contained 16 % organic material. The Young's modulus in the biological specimens was 9 GPa, whereas the synthetic spicules underwent aging, and the Young's modulus increased from 3 GPa for fresh spicules to 14 GPa and 19 GPa for one-month- and seven-month-old synthetic specimens, respectively. Hence, synthetic spicules can be considered to be twice as

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stiff as the biological ones. Furthermore, Natalio et al.[6] probed the fracture properties of the synthetic and natural specimens, and it turned out that the biological spicules were brittle and fractured similarly to a glass. Synthetic spicules, on the other hand, could not be fractured in the micromanipulator—even under extreme deflection—and exhibited elastic bending (Figure 2).

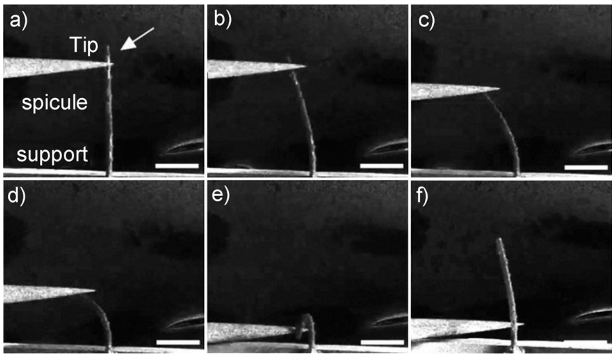

Figure 2. Time series (a–f) of SEM images illustrating a bending test with a micromanipulator. The synthetic calcitic spicule does not fracture even under extreme deflection, and shows a small plastic component upon release (f). Scale bars 50 µm. From Ref. [6]. Reprinted with permission from AAAS.

The work of Natalio et al.[6] is a significant and important step forward in bio-inspired materials syntheses. It shows that the transfer of principles and concepts from one system (silicatein-α/silica) to another—chemically rather distinct—combination (silicatein-α/calcium carbonate) does work and yields an unexpected material with unprecedented flexibility. This shows that general principles of biomineralization are not strictly limited in terms of chemistry, and can be utilized for the generation of new materials. Moreover, the material properties (specifically stiffness) in the synthetic spicules equal—or even surpass—that of the biological counterpart. The exact reason for this is not yet known but appears to be related to the mesocrystalline structure. In any case, this shows that superior material properties can indeed be achieved in artificial materials utilizing bio-inspired approaches, which has only rarely been achieved so far.[9,10] Importantly, in this case, the synthesis is realized by means of a facile approach that does not rely on harsh conditions or multiple-step procedures.

In particular, the extreme flexibility of the synthetic spicules is remarkable (Figure 2) and probably related to a high organic content (16 % vs. 1.5 % for the natural spicule). Indeed, a pronounced flexibility in mineral-based materials is required in many applications. Natalio et al.[6] have successfully demonstrated that the synthetic calcitic spicules could be utilized as optical fibers. Moreover, at macroscopic dimensions, micron-scale flexibility will almost certainly bring about superior fracture resistance with obvious ramifications for the design of flexible and strong mineral-based materials. For instance, the use of the spicules in fiber-reinforced concrete is a promising prospect.

It has to be noted, however, that proteins are difficult to produce in large quantities. This would almost certainly limit the potential use of the spicules in any economically viable application. For example, when it comes to optical fibers, cheaper silica- or plastic-based solutions dominate the market. Also, the micron-scale dimensions of the synthetic spicules appear to impair usability in most contexts, where large fibrils are required. From a scientific point of view, a crucial question is whether the outstanding flexibility of the artificial spicules relies on silicatein-α. Is it possible to obtain similar flexibility in hybrid materials utilizing low-cost polymers?

While it is clear that mesocrystalline structures with small nanodomains can be obtained utilizing truly artificial polymers,[5,8] the rather high organic content—which appears to be essential when it comes to flexibility—is rather unusual for mesocrystals of calcium carbonate and perhaps difficult to achieve with generic polymers. On the other hand, the cohesion of the organic matrix within the mesocrystal and its adhesion to the inorganic constituent are certainly also important for extreme flexibility. The inherent properties of the combination silicatein-α/calcium carbonate could include sacrificial bonds, hidden lengths, and potentially self-healing properties, which may or may not be attainable in combinations of calcium carbonate with artificial polymers. The major next step in bio-inspired materials chemistry is thus to realize the means to synthesize mesocrystals that rely on truly artificial, potentially bio-inspired polymers, and that can keep up with the stiffness and flexibility of the synthetic spicules of Natalio et al.[6]

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[1] H. Lowenstam, S. Weiner, *On Biomineralization*, Oxford University Press, New York, **1989**.
[2] M. A. Meyers, J. McKittrick, P.-Y. Chen, *Science* **2013**, *339*, 773–779.
[3] B. L. Smith, T. E. Schaffer, M. Viani, J. B. Thompson, N. A. Frederick, J. Kindt, A. Belcher, G. D. Stucky, D. E. Morse, P. K. Hansma, *Nature* **1999**, *399*, 761–763.
[4] H. J. Gao, B. H. Ji, I. L. Jäger, E. Arzt, P. Fratzl, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 5597–5600.
[5] F. C. Meldrum, H. Cölfen, *Chem. Rev.* **2008**, *108*, 4332–4432.
[6] F. Natalio, T. P. Corrales, M. Panthöfer, D. Schollmeyer, I. Lieberwirth, W. E. G. Müller, M. Kappl, H.-J. Butt, W. Tremel, *Science* **2013**, *339*, 1298–1302.
[7] R. L. Brutchey, D. E. Morse, *Chem. Rev.* **2008**, *108*, 4915–4934.
[8] H. Cölfen, M. Antonietti, *Angew. Chem.* **2005**, *117*, 5714–5730; *Angew. Chem. Int. Ed.* **2005**, *44*, 5576–5591.
[9] L. J. Bonderer, A. R. Studart, L. J. Gauckler, *Science* **2008**, *319*, 1069–1073.
[10] E. Munch, M. E. Launey, D. H. Alsem, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Science* **2008**, *322*, 1516–1520.